

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-034110

(43)Date of publication of application : 07.02.1997

(51)Int.Cl.

G03F 7/029
B41C 1/00
G03F 7/00
G03F 7/004
G03F 7/027
G03F 7/031
G03F 7/20

(21)Application number : 07-180086

(71)Applicant : KONICA CORP

(22)Date of filing : 17.07.1995

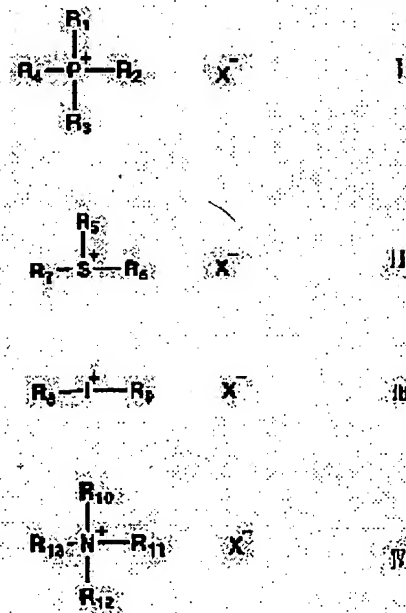
(72)Inventor : NAKAYAMA NORITAKA

(54) PHOTOPOLYMERIZABLE COMPOSITION, METHOD FOR GENERATING RADICAL, PHOTSENSITIVE MATERIAL FOR PRODUCING PLANOGRAPHIC PRINTING PLATE, AND PRODUCTION OF PLANOGRAPHIC PRINTING PLATE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a photopolymerizable compsn. having satisfactory preservability, capable of writing with IR and capable of forming an image having satisfactory resolution and sensitivity, to provide a method for generating radicals with IR highly sensitively, to obtain a photosensitive material having high photosensitivity in a near IR region as the oscillation wavelength region of semiconductor laser and excellent in shelf stability and to produce a planographic printing plate using the photosensitive material.

SOLUTION: This photopolymerizable compsn. contains a polymerizable compd., at least one of onium salts represented by general formulae I-IV, a photothermic conversion element and a radical generating agent on a substrate. In the formulae I-IV, each of R1-R4 and R10-R13 is alkyl, aryl or aralkyl, R1-R4 may bond to one another to form a ring, R10-R13 may bond to one another to form a ring, each of R5-R7 is alkyl or aryl, R5-R7 may bond to one another to form a ring, each of R8 and R9 is aryl and X⁻ is a counter anion.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the creation approach of the photopolymerization nature constituent and the radical generating approach of having used the onium salt (phosphonium salt, sulfonium salt, iodonium salt, ammonium salt), the light-and-heat sensing element, and the radical generating agent, the sensitive material for the lithography version creation, and the lithography version using it in more detail about the photopolymerization nature constituent and the radical generating approach using a new radical generating agent.

[0002]

[Description of the Prior Art] The image formation medium using the photopolymerization nature constituent which consists of an organic giant-molecule binder a polymerization nature compound, a photopolymerization initiator, a coloring agent, and if needed is indicated by JP,61-188537,A and 61-286858 as an object for creation of coloring images, such as a color proof. Generally these form the image which is eluted with a liquid in the unexposed section and consists of the exposure section after exposing a photosensitive layer in the image, and a photopolymerization initiator has visible spectral sensitivity from ultraviolet by combining with coloring matter.

[0003] Moreover, the photopolymerization initiator by the combination of a near-infrared color and a boron salt is known by JP,3-111402,A, 4-146905, and 4-362935. In these combination, although sensibility is high, its fluctuation of sensibility with the passage of time is large, and a problem is in preservation stability.

[0004] Furthermore, after irradiating ultraviolet rays at a bis-imidazole, making JP,43-19161,B generate a radical and making it color leuco coloring matter, the method to which an image is fixed by the visible ray is indicated. Although a bis-imidazole cleaving by ultraviolet rays generally, and generating a radical is known as shown in this approach, a radical is not generated only by combining with infrared coloring matter.

[0005] The approach of obtaining an image as another gestalt using the radical by the light or the pyrolysis of an onium salt is also reported. For example, although the method of obtaining an image by carrying out the polymerization of the monomer to Bull.Chem.Soc.Japan (Bull Tin OBU THE chemical society OBU Japan)43,567 (1970) using the radical generated by the pyrolysis of an onium salt is indicated, there is no publication used combining the light-and-heat conversion ingredient (light-and-heat sensing element said by this invention).

[0006] Moreover, many charges of a photosensitive lithography plate using a photopolymerization system and creation approaches of the lithography version of using it are learned.

[0007] Conventionally, as a photopolymerization initiator of the photopolymerization nature constituent used for these lithography version formation approaches, aromatic ketone, such as a benzophenone, a thioxan ton, a quinone, and thio acridone, a benzoin, benzyl, benzyl ketal, etc. are used. Since these photopolymerization initiators have the sensitization wavelength in an ultraviolet-rays field, after they stick a mask ingredient and expose it in sources of ultraviolet radiation, such as a mercury-vapor lamp,

they carry out elution development of the unexposed section.

[0008] In recent years, the sensitive material which has sensibility in the light of a long wave conventionally is demanded with the advance of an image processing, the light source, and an image formation technique. When one example is given, it is the picture signal and the output signal from a photoelectric process system or an image processing system which are transmitted by the communication line, and is the so-called direct platemaking system which modulates the light source, carries out direct-scanning exposure to sensitive material, and forms the printing version. As the light source at this time, laser is suitable. Especially, it was small and development of the charge of a photosensitive lithography plate which can carry out direct formation of the printing version in high resolution was desired using scan exposure of semiconductor laser of low cost.

[0009]

[Problem(s) to be Solved by the Invention] It succeeds in this invention that the trouble of the conventional technique should be improved. That is, the 1st object of this invention can do a store in infrared light, and is to offer the photopolymerization nature constituent which can form an image with good resolution and sensibility. The 2nd object is in offer of a photopolymerization nature constituent with good shelf life. The 3rd object is in offer of the radical generating approach of generating a radical in high sensitivity by infrared light. The 4th object is to offer the creation approach of the lithography version using the sensitive material for the lithography version creation and it which have high photosensitivity to the near infrared ray field which is an oscillation wavelength region of semiconductor laser, and were excellent in preservation stability.

[0010]

[Means for Solving the Problem] Wholeheartedly, as a result of examination, with the combination of a light-and-heat sensing element, an onium salt, and a radical generating agent, this invention persons find out the unexpected result that radical generating is possible, by high sensitivity, and came to complete this invention.

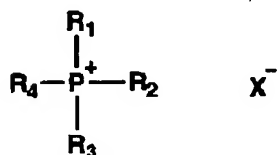
[0011] That is, the above-mentioned object of this invention is attained by the following configuration.

[0012] (1) The photopolymerization nature constituent containing at least one, light-and-heat sensing element, and radical generating agent of the onium salt expressed with a polymerization nature compound, the following general formula (I), (II), or (III) (IV) on a base material.

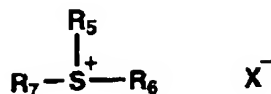
[0013]

[Formula 2]

一般式(I)



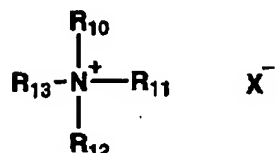
一般式(II)



一般式(III)



一般式(IV)



[0014] R1-R4, and R10-R13 express each, an alkyl group, an aryl group, or an aralkyl radical among a formula -- R1-R4, and R10-R13 -- each -- it may join together mutually and a ring may be formed. Respectively, R5, R6, and R7 express an alkyl group or an aryl group, and R5-R7 may join together mutually, and they may form a ring. R8 and R9 express an aryl group respectively, and X- expresses a pair anion.

[0015] (2) A photopolymerization nature constituent given in (1) whose a radical generating agent is a bis-imidazole derivative.

[0016] (3) A photopolymerization nature constituent given in (1) whose pair anion expressed with X- of said onium salt is halogen ion.

[0017] (4) An image formation ingredient given in (3) whose halogen ion is a chloride ion or bromine ion.

[0018] The radical generating approach which exposes the photopolymerization nature constituent of a publication by infrared light to (5) and (2).

[0019] (6) Sensitive material for the lithography version creation with which said sensitization layer contains at least one, light-and-heat sensing element, and radical generating agent of the onium salt expressed with the compound which has at least one ethylene nature unsaturated bond, a binder component, said general formula (I), (II), or (III) (IV) in the sensitive material for the lithography version creation which prepares a sensitization layer and a protective layer in this order at least, and changes on a hydrophilic base material.

[0020] The creation approach of the lithography version which carries out elution clearance of the unexposed section of a protective layer and a sensitization layer in the creation approach of the lithography version using a sensitive material for the lithography version creation given in (7) and (6) after semiconductor laser performs scan exposure in the image at the sensitization layer of said sensitive material.

[0021] Hereafter, this invention is explained more concretely.

[0022] First, the phosphonium salt compound (it is hereafter described as the phosphonium salt of this invention) expressed with a general formula (I) is explained in full detail.

[0023] As an example of a substituent expressed with R1-R4, it is as the following.

[0024] A straight chain and a branching alkyl group are contained as an alkyl group, for example, methyl, ethyl, butyl, i-butyl, hexyl, octyl, a stearyl radical, etc. are mentioned. The alkyl group of the point of coloring concentration to the carbon numbers 1-10 is desirable, and especially butyl is desirable. It may join together mutually, these alkyl groups may form a ring, and its things (for example, cyclopentyl, a cyclohexyl radical, etc.) of five to 7 membered-ring are desirable as a cycloalkyl radical.

[0025] Phenyl, a naphthyl group, etc. are mentioned as an aryl group, and benzyl, a phenethyl radical, etc. are mentioned as an aralkyl radical.

[0026] These radicals may be permuted further and a halogen atom, a cyano group, a nitro group, an alkyl group, an aryl group, hydroxyl, the amino group (the alkylation amino group is included), an alkoxy group, a carbamoyl group, -COOR radical, and -OCOR radical (R is organic radicals, such as an alkyl group and an aryl group) are mentioned as a substituent.

[0027] Although it will not be restrained as a pair anion expressed with X- especially if it is a univalent anion, it is halogen ion preferably and chlorine and a bromine anion are still more desirable in respect of coloring concentration. as the example of a pair anion -- a star's picture, chloride, iodide, and a full ora -- the id, perchlorate, benzoate, thio cyanate, acetate, trifluoroacetate, hexafluorophosphate, a nitrate, SARISHINETO, etc. are mentioned.

[0028] Next, the sulfonium salt compound (it is hereafter described as the sulfonium salt of this invention) expressed with a general formula (II) is explained in full detail.

[0029] As an example of a substituent expressed with R5-R7, it is as the following.

[0030] A straight chain and a branching alkyl group are contained as an alkyl group, and methyl, ethyl, butyl, i-butyl, hexyl, octyl, a stearyl radical, etc. are mentioned. The alkyl group of the point of coloring concentration to the carbon numbers 1-10 is desirable, and especially butyl is desirable. It may join together mutually, these alkyl groups may form a ring, and its things (for example, cyclopentyl, a cyclohexyl radical, etc.) of five to 7 membered-ring are desirable as a cycloalkyl radical.

[0031] Phenyl, naphthyl, etc. are mentioned as an aryl group.

[0032] A benzothia thio pyrylium ring etc. is mentioned as a ring which R5-R7 combine mutually, and they form with S+.

[0033] These radicals may be permuted further and the radical stated by said general formula (I) and the same radical are mentioned as a substituent.

[0034] The pair anion expressed with X- is synonymous with X- of a general formula (I).

[0035] Furthermore, the iodonium salt compound (it is hereafter described as the iodonium salt of this invention) expressed with a general formula (III) is explained in full detail.

[0036] Although phenyl, a naphthyl group, etc. are mentioned as an aryl group expressed with R8 and R9, these radicals may be permuted further and the radical stated by said general formula (I) and the same radical are mentioned as a substituent.

[0037] The pair anion expressed with X- is synonymous with X- of a general formula (I).

[0038] Next, the ammonium salt compound (it is hereafter described as the ammonium salt of this invention) expressed with a general formula (IV) is explained in full detail.

[0039] As an example of a substituent expressed with R10-R13, it is as the following.

[0040] A straight chain and a branching alkyl group are contained as an alkyl group, for example, methyl, ethyl, butyl, i-butyl, hexyl, octyl, stearyl, etc. are mentioned. The alkyl group of the point of coloring concentration to the carbon numbers 1-10 is desirable, and especially butyl is desirable. It may join together mutually, these alkyl groups may form a ring, and its things (for example, cyclopentyl, a cyclohexyl radical, etc.) of five to 7 membered-ring are desirable as a cycloalkyl radical.

[0041] Phenyl, a naphthyl group, etc. are mentioned as an aryl group, and benzyl, a phenethyl radical, etc. are mentioned as an aralkyl radical.

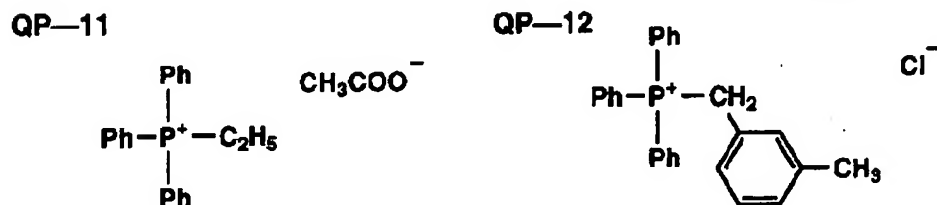
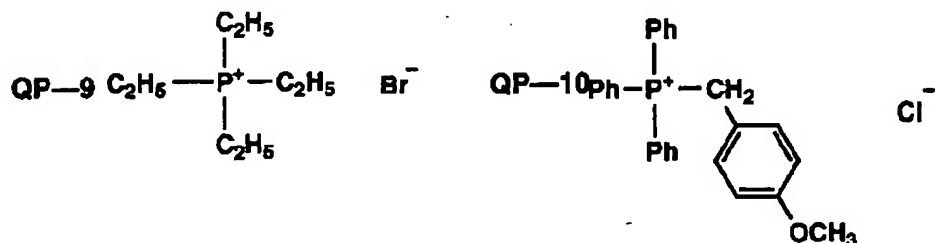
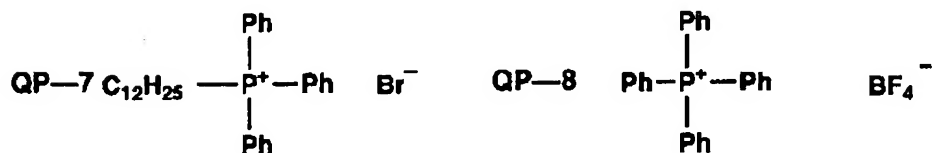
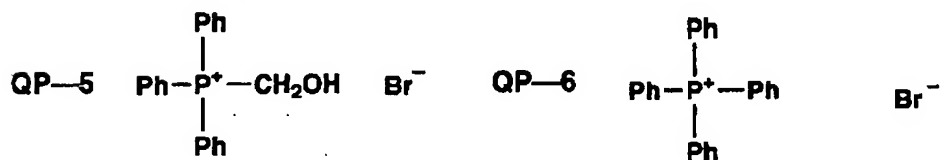
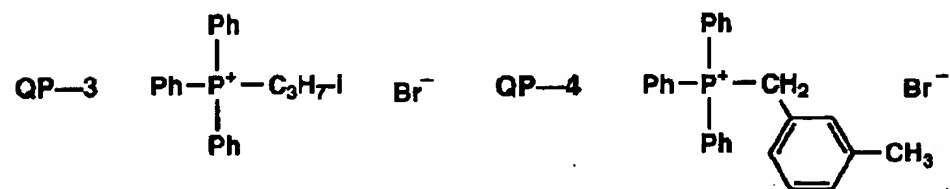
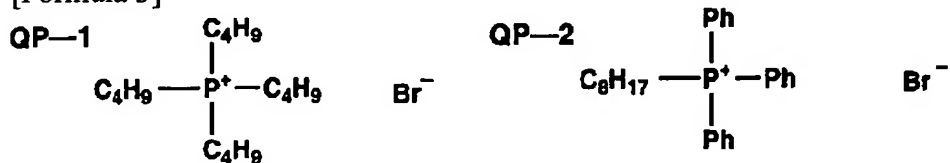
[0042] These radicals may be permuted further and a halogen atom, a cyano group, a nitro group, an alkyl group, an aryl group, hydroxyl, the amino group (the alkylation amino group is included), an

alkoxy group, a carbamoyl group, -COOR radical, and -OCOR (R is organic radicals, such as an alkyl group and an aryl group) are mentioned as a substituent.

[0043] Although the typical example of the onium salt of this invention is given to below, it is not limited to these.

[0044]

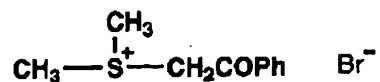
[Formula 3]



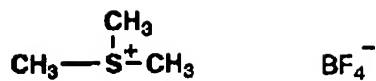
[0045]

[Formula 4]

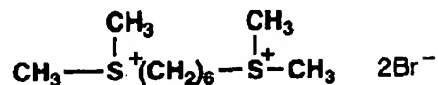
QS-1



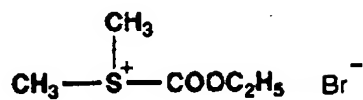
QS-2



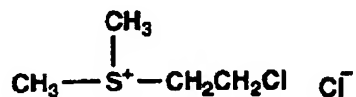
QS-3



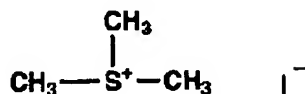
QS-4



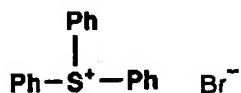
QS-5



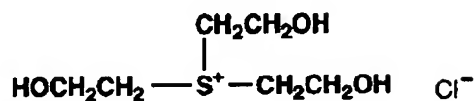
QS-6



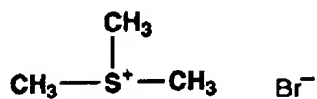
QS-7



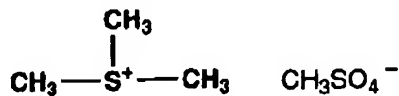
QS-8



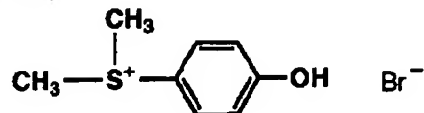
QS-9



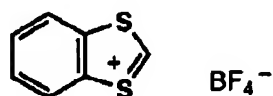
QS-10



QS-11

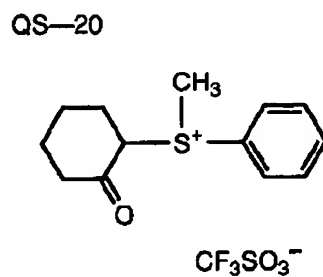
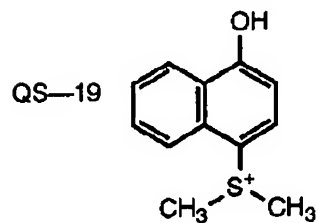
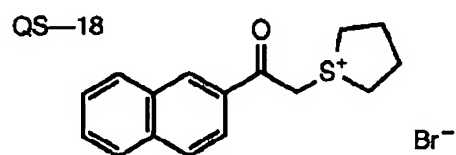
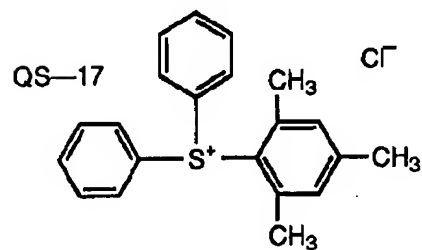
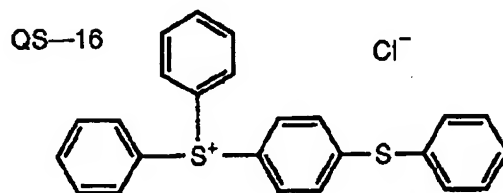
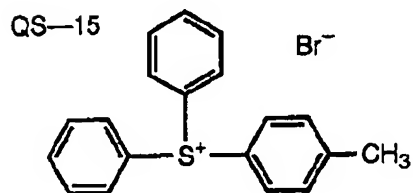
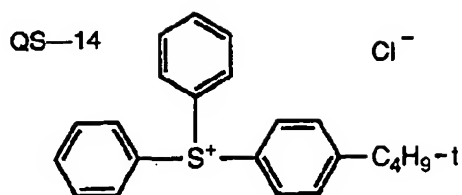
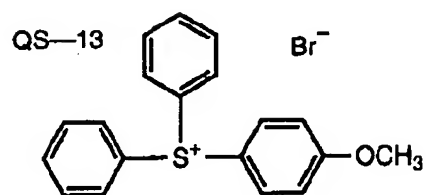


QS-12



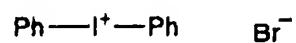
[0046]

[Formula 5]



[0047]
[Formula 6]

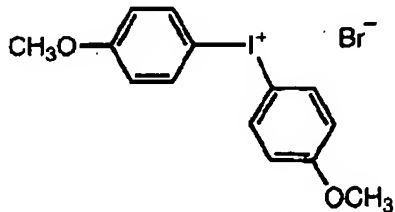
QI-1



QII-2



QI-3



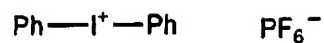
QI-4



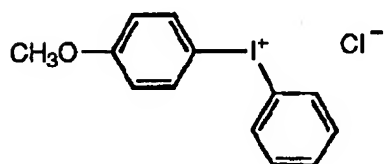
QI-5



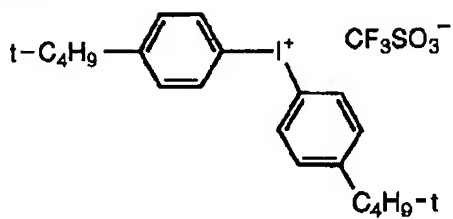
QI-6



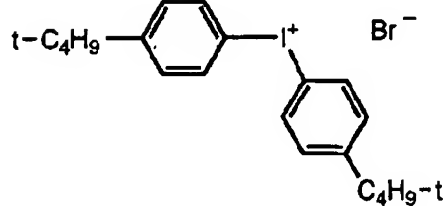
QI-7



QI-8

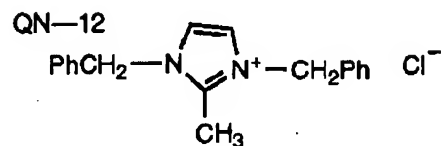
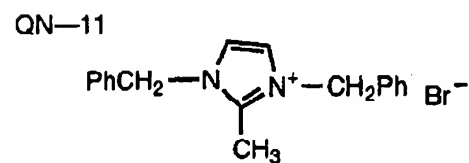
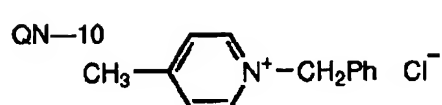
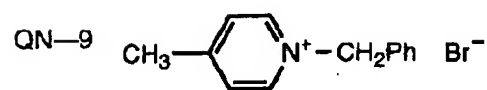
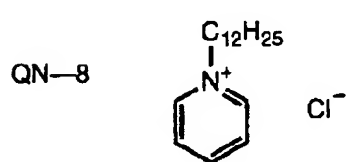
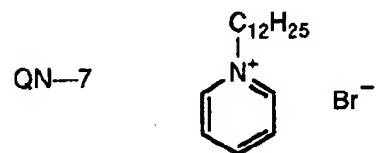
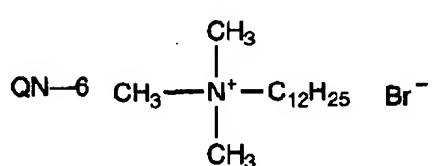
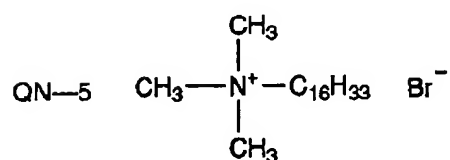
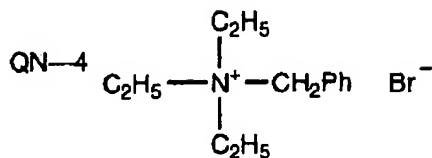
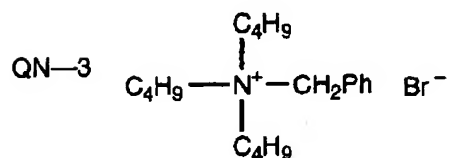
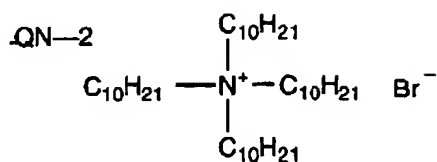
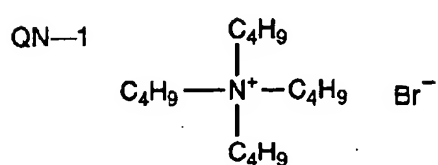


QI-9



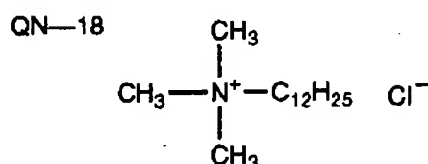
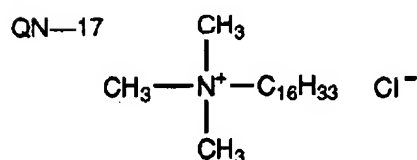
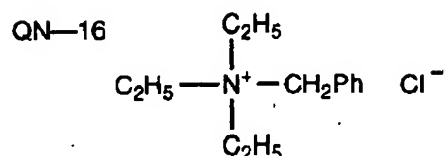
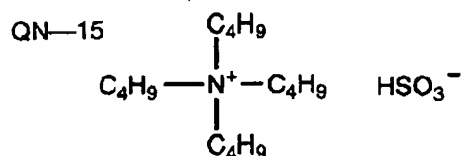
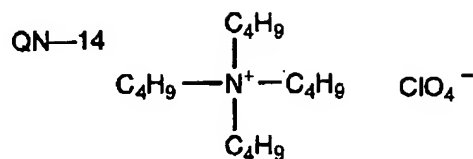
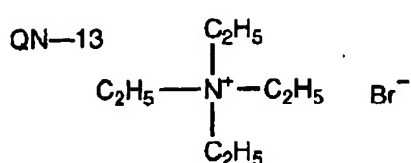
[0048]

[Formula 7]



[0049]

[Formula 8]



構造式中の Ph はフェニル基を示す。

[0050] Although the addition of the onium salt of this invention changes with the classes and activity gestalten of an onium salt, per [0.2-5g] two are [1m of image formation ingredients] desirable.

[0051] Next, a light-and-heat sensing element is explained in full detail.

[0052] When using semiconductor laser as the light source, as for the light-and-heat sensing element used for this invention, what has absorption in near-infrared is [that what is necessary is just the matter which absorbs light and is efficiently changed into heat] desirable. For example, carbon black, magnetic powder, and a black color can be used for various cyanine dye, an anthraquinone system, the India aniline metal complex system, an AZURENIUMU system, a crocodile NIUMU system, a squarylium system, a dithiol metal complex system, a chelate system, a naphthalocyanine metal complex system, intermolecular CT system coloring matter, etc. as an infrared color at first. Although it is compoundable by the well-known approach as well as these coloring matter, the following commercial items can also be used.

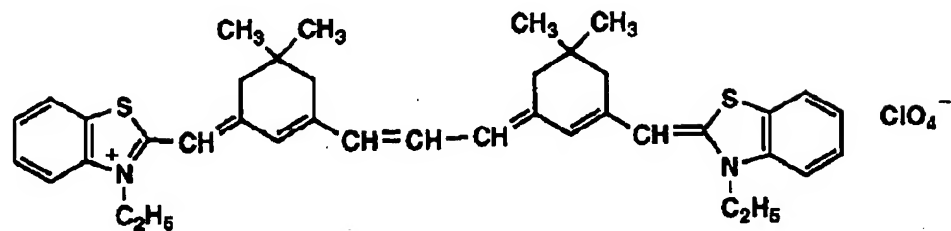
[0053] Nippon Kayaku : IR750 ; IR002, IR003 (Anthraquinone system) ; IR820 (Aluminum system) ; IRG022, IRG033 (Poly methine system) (Gene MONIUMU system); -- CY- 2, CY-4, CY-9, CY-20, Mitsui Toatsu Chemicals; KIR103, and SIR103(phthalocyanine system); -- KIR101 and SIR114 (anthraquinone system) ;P A1001, PA1005, PA1006, and SIR128 (metal complex system) -- Dainippon Ink chemistry; Fastogen 1011 blue8120, green chemistry; MIR-101, 1021.

[0054] The example of a typical compound of the light-and-heat sensing element preferably used for below is given.

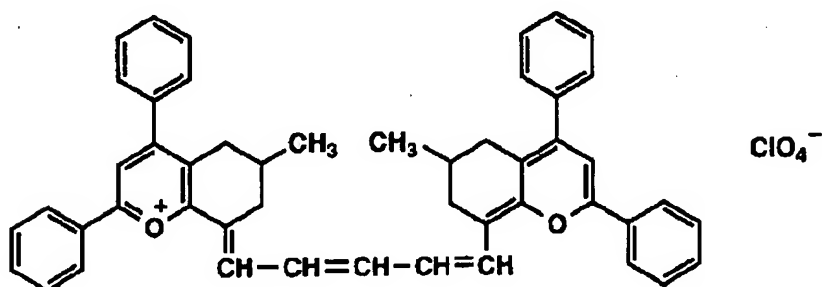
[0055]

[Formula 9]

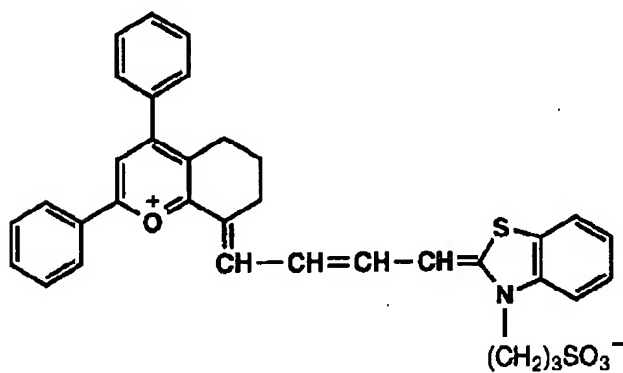
IR-1



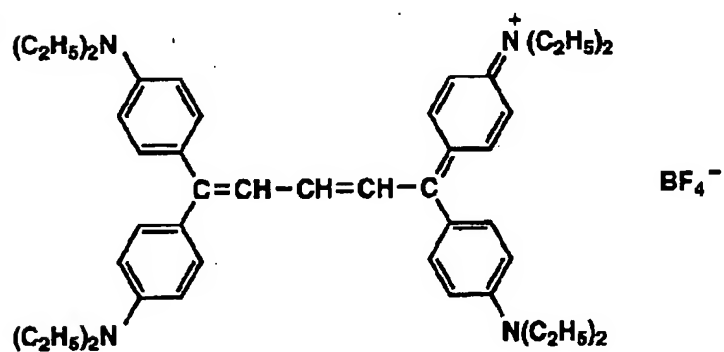
IR-2



IR-3



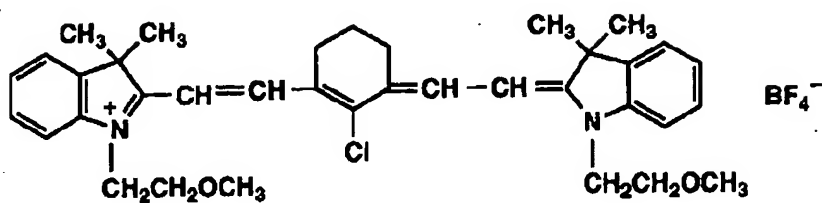
IR-4



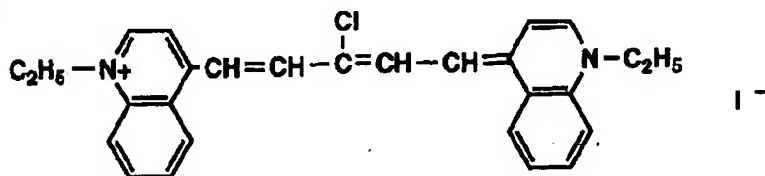
[0056]

[Formula 10]

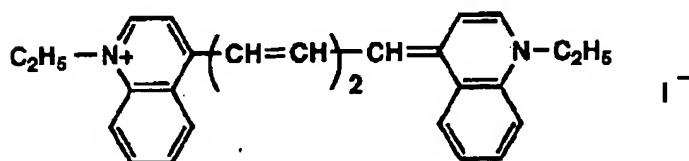
IR-5



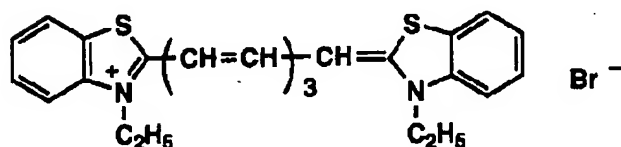
IR-6



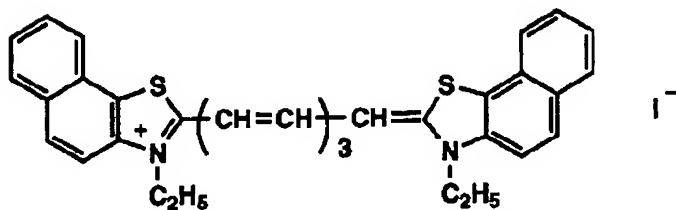
IR-7



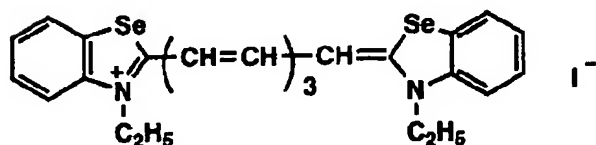
IR-8



IR-9



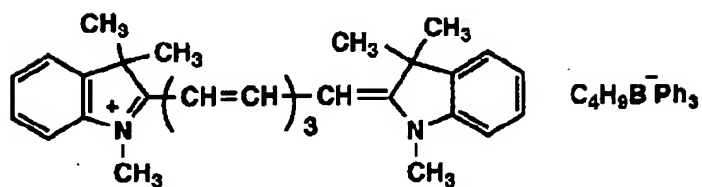
IR-10



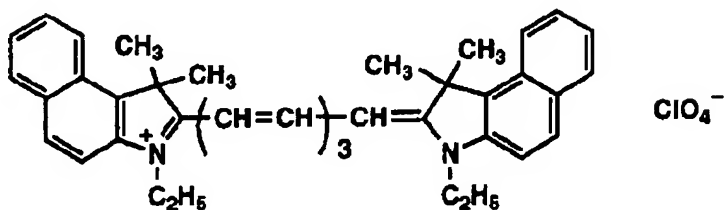
[0057]

[Formula 11]

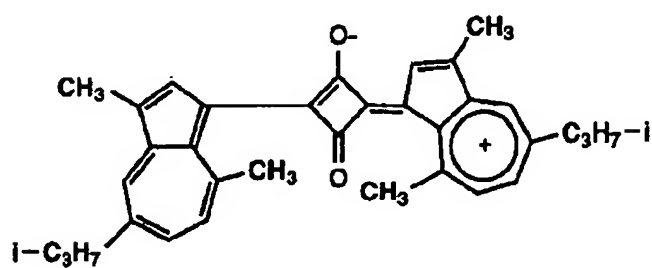
IR-11



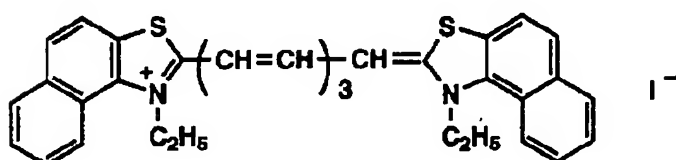
IR-12



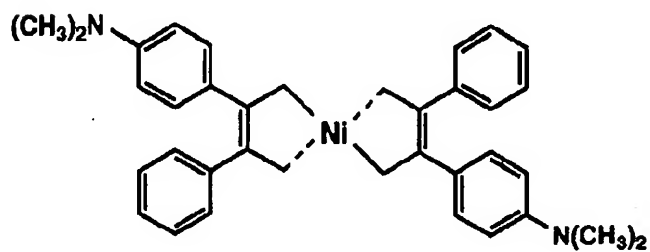
IR-13



IR-14



IR-15



[0058]

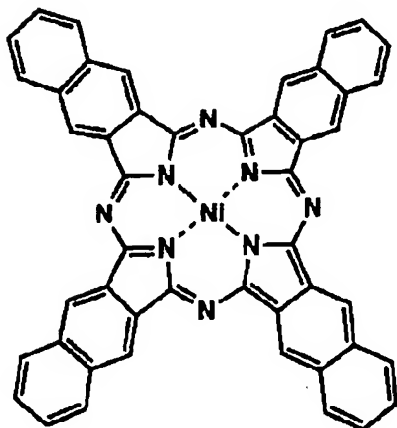
[Formula 12]

CN1c2ccccc2c3ccccc13C=CC=CC=CC=CC=N4c5ccccc5c6ccccc46CC(=O)Nc1ccc(cc1)/C=C2C(=C(C#N)C#N)C(=C(C#N)C#N)c3ccccc23CN(C)c1ccc(N=C2C=CC3C(=C2)C=CC=C3C(=O)N(C)C)cc1CCCSC(=O)c1ccc(NC(=O)c2c3ccccc3c(=O)c2=Nc4cc(C)c(NCC)c4C)c1CN(C)c1ccc(N2C(=O)c3c(C)c(=N4C(=O)N(c5ccccc5)N=C4N3)C2=O)cc1C

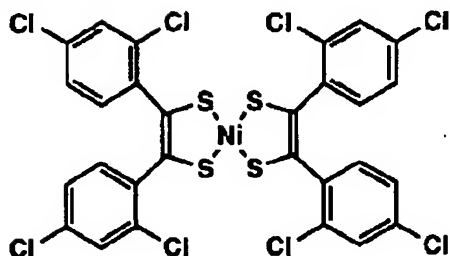
[0059]

[Formula 13]

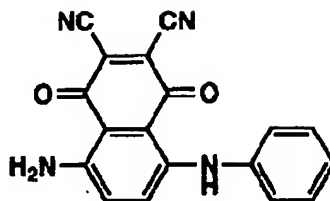
IR—23



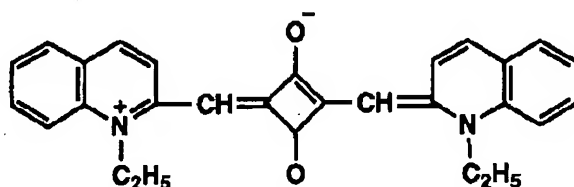
IR—24



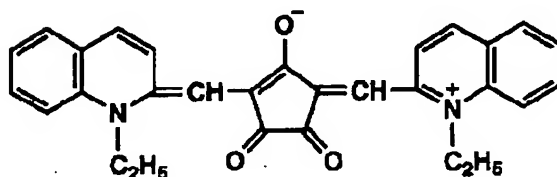
IR—25



IR—26



IR—27



[0060] Although a solid content presentation is 20 - 70 % of the weight preferably two to 80% of the weight and adding in a radical initiator and this layer is usually desirable as for the addition of a light-and-heat sensing element, when it consists of two or more layers, it may be added in another layer.

[0061] Next, a radical generating agent is explained.

[0062] If the format of this invention is followed, heat occurred from the light-and-heat sensing element by infrared light, and I think with heat that a radical is generated by the interaction of the onium salt which is the description of this invention, and a radical generating agent.

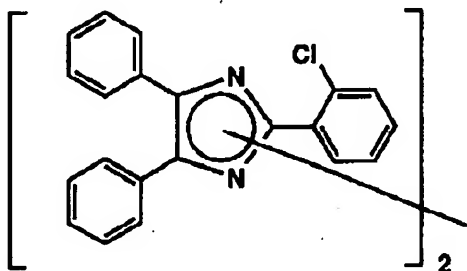
[0063] As a radical generating agent, although halogenides, such as alpha-halo acetophenones and

TORIKURORO methyl triazine, an azo compound, aromatic series carbonyl compounds, such as benzoin ester, ketals, acetophenones, o-acyloxy imino ketones, and acyl phosphine oxide, a hexa aryl bis-imidazole compound, a peroxide, etc. are mentioned concretely, it is a bis-imidazole derivative preferably. Although an example is shown below, it is not restricted to these.

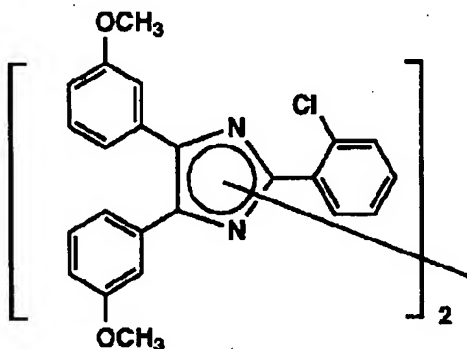
[0064]

[Formula 14]

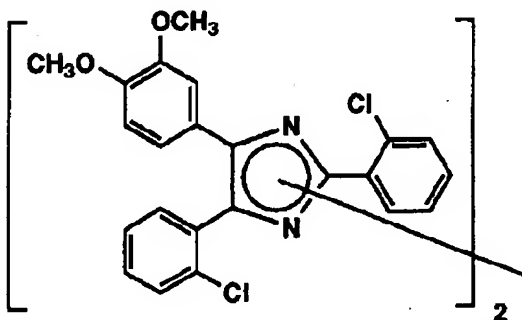
A—1



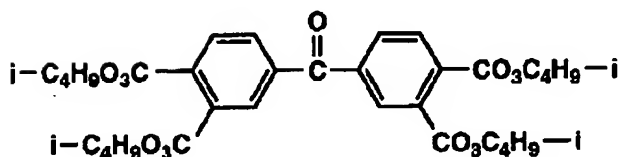
A—2



A—3



A—4



[0065] Although the addition of the radical generating agent of this invention changes with the classes and activity gestalten of a radical generating agent, per [0.1-10g] two are [1m of image formation ingredients] desirable.

[0066] A sensitization layer applies on a base material, and it dries suitably and it forms the sensitization layer coating liquid which distributed to the dissolution in the solvent, it made distribute an onium salt, a

radical generating agent, and a light-and-heat sensing element in the shape of a particle in a solvent with a binder, and was prepared. The thickness of a sensitization layer has desirable 5-100 micrometers at desiccation thickness.

[0067] A film or a sheet etc. which carried out the laminating of the resin layer to the paper milled by the film of paper, a synthetic paper (for example, synthetic paper which uses polypropylene as a principal component), and resin or a sheet, the plastic film that comes to carry out the laminating of the resin more than two-layer further, a sheet or various polymeric materials, the metal, the ceramic or wood pulp, cellulose pulp, a sulfite pulp, etc. as a base material can be mentioned. As resin which constitutes the film or sheet of such resin Acrylic resin, such as acrylic ester and methacrylic ester, polyethylene terephthalate, Polybutylene terephthalate, polyethylenenaphthalate, a polycarbonate, Polyester system resin, such as polyarylate, a polyvinyl chloride, a polyvinylidene chloride, Polyolefine system resin, such as polyvinylidene fluoride, polyethylene, polypropylene, and polystyrene, Polyamide system resin, such as nylon and aromatic polyamide, a polyether ether ketone, Polysulfone, polyether sulphone, polyimide, polyether imide, Pori parabanic acid, phenoxy resin, an epoxy resin, urethane resin, melamine resin, an alkyd resin, phenol resin, fluororesin, silicone resin, etc. are mentioned.

[0068] As a base material which prepares the sensitization layer in the case of using as an object for the lithography version creation, the paper in which metallic foils, such as paper in which metal plates, such as aluminum, zinc, copper, and steel, the metal plate with which chromium, zinc, copper, nickel, aluminum, iron, etc. were plated or vapor-deposited by the list, paper, a plastic film and a glass plate, and resin were applied, and aluminum, be stretched, the plastic film which carried out hydrophilization processing be mentioned. An aluminum plate is [among these] desirable.

[0069] It is more desirable to use the aluminum plate with which surface treatment, such as sealing, was performed as a base material of this invention graining processing, anodizing, and if needed.

[0070] A well-known approach can be used for these processings. As the approach of graining processing, the approach of etching, for example by the mechanical approach and electrolysis is mentioned. As the mechanical approach, the ball grinding method, a brushing method, the grinding method by liquid honing, and buffing are mentioned, for example.

[0071] independent [in various above-mentioned approaches] according to the presentation of aluminum material etc. -- or it can combine and use. The approach by electrolytic etching is desirable.

[0072] Electrolytic etching is performed by the independent bath of acids, such as phosphoric acid, a sulfuric acid, a hydrochloric acid, and a nitric acid, which it was, and was carried out and was mixed two or more sorts. After graining processing, if needed, with the water solution of alkali or an acid, a desmut treatment is performed, and it neutralizes and rinses. A sulfuric acid, a chromic acid, oxalic acid, phosphoric acid, a malonic acid, etc. are carried out to anodizing by electrolyzing as an anode plate in an aluminum plate, using one sort or the solution included two or more sorts as the electrolytic solution. 1 - 50 mg/dm² is suitable for the formed amount of anodic oxide films, and it is 10 - 40 mg/dm² preferably. The amount of anodic oxide films dips an aluminum plate in a phosphoric acid chromic-acid solution, dissolves an oxide film, and is calculated from the weight change measurement before and behind the coat dissolution of a plate etc.

[0073] As for sealing, ebullition water treatment, steam treatment, specific silicate processing, dichromate water-solution processing, etc. are mentioned as an example. In addition, undercoating processing by metal salt water solutions, such as a water soluble polymer compound and fluoridation zircon, can also be performed to an aluminum plate base material.

[0074] The thickness of a base material usually has desirable 3-1000 micrometers, and its 8-300 micrometers are more desirable.

[0075] Well-known various polymers can be used as binder resin used for a sensitization layer. The detail of a concrete binder is indicated by the U.S. Pat. No. 4,072,527 number. The monomer which has the **** aromaticity hydroxyl group more preferably indicated by JP,54-98613,A, For example, N-(4-hydroxyphenyl) acrylamide, N-(4-hydroxyphenyl) methacrylamide, The copolymerization object of o-, m- or p-hydroxystyrene, o-, m-, or p-hydroxyphenyl methacrylate etc. and other monomers, The polymer containing a hydroxyethyl acrylate unit or hydroxyethyl methacrylate which is indicated in a

U.S. Pat. No. 4,123,276 number, Natural resin, such as a shellac and rosin, polyvinyl alcohol, polyamide resin that is indicated in a U.S. Pat. No. 3,751,257 number, a line which is indicated in a U.S. Pat. No. 3,660,097 number -- polyurethane resin -- Cellulosic resin, such as phthalate-ized resin of polyvinyl alcohol, an epoxy resin by which condensation was carried out from bisphenol A and epichlorohydrin, cellulose acetate, and cellulose acetate phthalate, etc. is mentioned.

[0076] As binder resin, it can use combining one sort or two sorts or more of things out of these resin. Solvent fusibility polymers, such as vinyl chloride and vinyl chloride-vinyl acetate copolymerization resin, acrylic resin, methacrylic resin, polystyrene, a polycarbonate, polysulfone, polyether sulphone, a polyvinyl butyral, styrene-acrylonitrile, a polyvinyl acetal, a nitrocellulose, and ethyl cellulose, are desirable especially.

[0077] These binders not only dissolve and use one sort or two sorts or more for an organic solvent, but you may use them in the form of latex distribution. Although it differs by whether it is a monolayer configuration or it is a multistory configuration as amount of the binder used, corresponding to the object of the image formation ingredient of this invention, per [1.0-20g] two are [1m of base materials] desirable.

[0078] Next, a polymerization nature compound is explained in full detail.

[0079] A monomer well-known as a compound in which a polymerization is possible can use it without a limit especially. As a concrete monomer, for example 2-ethylhexyl acrylate, Monofunctional acrylic ester and its derivative, or these acrylate, such as 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate, methacrylate, The compound replaced with itaconate, crotonate, maleate, etc.; Polyethylene-glycol diacrylate, Pentaerythritol diacrylate, bisphenol A diacrylate, 2 organic-functions acrylic ester and its derivative, or these acrylate of epsilon-caprolactone addition product of hydroxy pivalate neopentyl glycol, such as diacrylate, methacrylate, Compound; or TORIMECHI roll pro pantry (meta) acrylate replaced with itaconate, crotonate, maleate, etc., Dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, The compound which replaced polyfunctional acrylic ester and its derivative, or these acrylate, such as a pyrogallol thoria chestnut rate, with methacrylate, itaconate, crotonate, maleate, etc. can be mentioned. Moreover, an acrylic acid or methacrylic acid is introduced into the oligomer of suitable molecular weight, and what is called the so-called prepolymer which gave photopolymerization nature can be used suitably.

[0080] In addition, the compound of a publication etc. can be mentioned to JP,58-212994,A, 61-6649, 62-46688, 62-48589, 62-173295, 62-187092, 63-67189, JP,1-244891,A, etc., and the compound of the compound of "chemistry goods of 11290" Chemical Daily and a 286-294-page publication, a "UV-EB hardening handbook (volume on raw material)" macromolecule publication meeting, and a 11-65-page publication etc. can be used further suitably.

[0081] In these, the compound which has two or more acrylic radicals or methacrylic radicals in intramolecular is desirable in this invention, and 5,000 or less thing has [10,000 or less] more preferably more desirable still molecular weight. Moreover, in this invention, one sort or two sorts or more in these monomers or a prepolymer can be mixed and used.

[0082] The compound which has an ethylene nature partial saturation radical is more preferably contained 30 to 60% of the weight 20 to 80% of the weight in a sensitization layer.

[0083] The sensitive material for the lithography version creation (it is also only hereafter called sensitive material) may have auxiliary layers other than the sensitization layer containing a light-and-heat conversion ingredient, such as an interlayer, a protective layer, and an undercoating layer.

[0084] Next, the image formation approach using the sensitive material of this invention is explained. If sensitive material is exposed in the image, according to light exposure, heat will occur with a light-and-heat conversion ingredient, a radical generating agent and an onium salt interact with this heat, and a radical generates. When it uses for the ingredient which carries out image formation by the radical polymerization, a polymerization happens by the generated radical and an image is formed. Sunlight, tungsten light, a mercury lamp, a halogen lamp, a xenon lamp, laser light, light emitting diode, CRT, etc. can be used for exposure to sensitive material. As an ingredient which carries out image formation by the above-mentioned radical polymerization, the coloring agent is contained the compound which has an

ethylene nature unsaturated bond at least and in which a polymerization is possible, and if needed in the photosensitive layer. As a compound which has such an ethylene nature unsaturated bond and in which a polymerization is possible, the well-known monomer which can construct a bridge can use it without a limit especially. As a concrete monomer, for example 2-ethylhexyl acrylate, Monofunctional acrylic ester and its derivative, or these acrylate, such as 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate, methacrylate, The compound replaced with itaconate, crotonate, maleate, etc., polyethylene-glycol diacrylate, Pentaerythritol diacrylate, bisphenol A diacrylate, 2 organic-functions acrylic ester and its derivative, or these acrylate of epsilon-caprolactone addition product of hydroxy pivalate neopentyl glycol, such as diacrylate, methacrylate, The compound replaced with itaconate, crotonate, maleate, etc., or TORIMECHI roll pro pantry (meta) acrylate, Dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, The compound which replaced polyfunctional acrylic ester and its derivative, or these acrylate, such as a pyrogallol thoria chestnut rate, with methacrylate, itaconate, crotonate, maleate, etc. can be mentioned. Moreover, the resin which has an ethylene nature unsaturated bond introduces an acrylic acid or methacrylic acid into the oligomer of suitable molecular weight, and the thing which gave photopolymerization nature and which is called the so-called prepolymer can also be suitably used for it. In addition, the compound of a publication etc. can be mentioned to JP,58-212994,A, 61-6649, 62-46688, 62-48589, 62-173295, 62-187092, 63-67189, JP,1-244891,A, etc., and the compound of "the chemistry goods of 11290" (above), the compound of a 286-294-page publication, "a UV-EB hardening handbook (volume on raw material)" (above), and a 11-65-page publication etc. can be further used for them suitably in this invention. In these, the compound which has two or more acrylics or methacrylic radicals in intramolecular is desirable in this invention, and 5,000 or less thing has [10,000 or less] more preferably more desirable still molecular weight. Moreover, in this invention, one sort or two sorts or more in these monomers or a prepolymer can be mixed and used.

[0085] As for the compound which has an ethylene nature unsaturated bond and in which a polymerization is possible, it is usually desirable among a photosensitive stratification constituent to carry out to 15% of the weight or more more preferably 5% of the weight or more.

[0086] Binder resin is used for a sensitization layer if needed. As binder resin, polyester system resin, polyvinyl-acetal system resin, polyurethane system resin, polyamide system resin, cellulose type resin, olefin system resin, vinyl chloride system resin, acrylic (meta) resin, styrene resin, a polycarbonate, polyvinyl alcohol, a polyvinyl pyrrolidone, polysulfone, poly caprolactone resin, polyacrylonitrile resin, a urea-resin, an epoxy resin, phenoxy resin, rubber system resin, etc. are mentioned. Moreover, since it is possible to carry out a polymerization to the compound which has the above-mentioned ethylene nature unsaturated bond, the resin which has an unsaturated bond in resin, for example, diallyl phthalate resin, its derivative, chlorination polypropylene, etc. can be suitably used according to an application. As binder resin, it can use combining one sort or two sorts or more of things out of the above-mentioned resin.

[0087] As for these binder resin, it is desirable to use it in the range below the 200 weight sections more preferably below the 500 weight sections to the compound 100 weight section which has said ethylene nature unsaturated bond and in which a polymerization is possible.

[0088] A coloring agent may color as one gestalt of this invention. The coloring agent is constituted so that the absorbance (an absorbance means a transmittance factor density in this invention) of the point of arbitration may become 3.0 or more in the wavelength range of at least 350-700nm. This coloring agent is contained in a sensitization layer.

[0089] A sensitization layer is made to contain a pigment and/or a color with carbon black, titanium oxide, an iron oxide, phthalocyanine pigment, azo pigment, an anthraquinone system pigment, the Quinacridone system pigment, well-known crystal violet, methylene blue, azo system color, anthraquinone system color, cyanine system color, etc. as a coloring agent, combining one sort or two sorts or more so that the above-mentioned absorbance may be satisfied.

[0090] As an addition of a coloring agent, among a sensitization layer or a color-material stratification constituent, 10 - 80 % of the weight is desirable, and is 15 - 70 % of the weight more preferably.

[0091] What is necessary is just to use coating liquid in sensitization layer constituents other than a

coloring agent, using the equipment of official businesses, such as a sand mill, a ball mill, attritor, an ultrasonic disperser, a jet mill, a homogenizer, and a planetary mill, doing distribution and mixing of a coloring agent, and filtering if needed further, in order to make a coloring agent add into a sensitization layer or a color-material layer.

[0092] It is arbitrary to make the sensitization layer concerning this invention contain other components, such as a sensitizer, thermal polymerization inhibitor, a thermofusion nature compound, an oxygen supplement agent, and a plasticizer, in the range which does not spoil the object.

[0093] As a sensitizer, organic peroxide given in triazine compound given in JP,64-13140,A, an aromatic series onium salt given in JP,64-13141,A, an aromatic series halo NIUMU salt, and JP,64-13143,A, a bis-imidazole compound given in JP,45-37377,B or a U.S. Pat. No. 3,652,275 number, thiols, etc. are mentioned. 0.01-5 weight section extent addition of the addition of a sensitizer is preferably carried out below 10 weight sections to the total quantity 100 weight section of the compound in which a polymerization is possible, and a binder which has an ethylene nature unsaturated bond.

[0094] As a thermal polymerization inhibitor, compounds, such as a quinone system and a phenol system, are used preferably. For example, hydroquinone, pyrogallol, p-methoxy phenol, a catechol, the beta-naphthol, 2,6-di-t-butyl-p-cresol, etc. are mentioned. 0.01-5 weight section extent addition is preferably carried out below 10 weight sections to the total quantity 100 weight section of the compound in which a polymerization is possible, and a binder which has an ethylene nature unsaturated bond.

[0095] As an oxygen quencher, N and N-dialkyl aniline derivative is desirable, for example, the compound of a publication is mentioned [the 11 columns of the 58th line of a U.S. Pat. No. 4,772,541 number - 12 column / of the 35th line].

[0096] As a plasticizer, phthalic ester, trimellitic acid ester, adipate, other saturation or unsaturated-carboxylic-acid ester, citric acid ester, epoxidized soybean oil, epoxidation linseed oil, stearin acid epoxy, orthophosphoric acid ester, phosphite, and glycol ester are mentioned.

[0097] As a thermofusion nature compound, it is a solid-state in ordinary temperature, and the compound which serves as a liquid reversibly at the time of heating is used. As said thermofusion nature matter, a terpeneol, menthol, 1, 4-cyclohexane diol, Alcohols, such as a phenol; Amides; coumarins, such as an acetamide and a benzamide, Ester, such as benzyl cinnamate; Ether; camphor, such as diphenyl ether and crown ether, Ketones, such as p-methyl acetophenone; Aldehydes; norbornene, such as a vanillin and a dimethoxy benzaldehyde, hydrocarbons [such as a stilbene,]; -- higher-fatty-acids [such as margaric acid]; -- higher-alcohol [such as eicosa Norian,]; -- higher-fatty-acid ester [such as cetyl palmitate]; -- higher-fatty-acid amides [such as octadecanamide]; -- the single molecular compound represented by high-class amines, such as a behenyl amine, etc. and beeswax -- A candelilla wax, paraffin wax, ester wax, montan wax, Waxes, such as carnauba wax, an amide wax, polyethylene wax, and a micro crystallin wax Rosin derivatives, such as rosin ester, rosin maleic resin, and rosin phenol resin, Phenol resin, ketone resin, an epoxy resin, diallyl phthalate resin, The high molecular compound represented by polyolefine oxide, such as terpene system hydrocarbon resin, cyclopentadiene resin, polyolefine system resin, poly caprolactone system resin, a polyethylene glycol, and a polypropylene glycol, etc. can be mentioned.

[0098] Furthermore, in a photosensitive layer, an antioxidant, a filler, and antistatic-agent ***** may be added if needed.

[0099] As an antioxidant, a chroman system compound, a KURAMAN system compound, a phenol system compound, a hydroquinone derivative, a hindered amine derivative, a SUPIRO in out system compound, a sulfur system compound, a phosphorus system compound, etc. are mentioned, and a compound well-known as what improves endurance can be mentioned to a compound given in JP,59-182785,A, 60-130735, 61-159644, JP,1-127387,A, "the chemistry goods of 11290" (above), 862-868 etc. pages, etc., and the image recording ingredient of a photograph and others.

[0100] As a filler, a non-subtlety particle and an organic resin particle can be mentioned. As a non-subtlety particle, silica gel, a calcium carbonate, titanium oxide, a zinc oxide, A barium sulfate, talc, clay, a kaolin, the acid clay, the activated clay, an alumina, etc. can be mentioned. As an organic particle As resin particles, such as a fluororesin particle, a guanamine resin particle, an acrylic resin particle, and

a silicon resin particle, and an antistatic agent The compound of a publication can also be suitably used for "the chemistry goods of 11290" (above) besides being a cation system surfactant, an anion system surfactant, a nonionic surfactant, a macromolecule antistatic agent, a conductive particle, etc., 875-876 etc. pages, etc.

[0101] In this invention, a sensitization layer may be formed by the monolayer and may consist of two or more layers more than two-layer. Moreover, when it constitutes from two or more layers, you may constitute from a photosensitive layer from which a presentation differs, and the sensitization layer which does not contain a coloring agent in this case may be included.

[0102] The thickness of a sensitization layer has desirable 0.2-10 micrometers, and it is 0.5-5 micrometers more preferably.

[0103] A sensitization layer distributes or dissolves a formation component in a solvent, prepares coating liquid, on the cover sheet which carries out direct laminating spreading, and dries on said middle class, or is mentioned later, is applied, and is dried and formed.

[0104] As a solvent used for a coating method, water, alcohols (ethanol, propanol, etc.), cellosolves (methyl cellosolve, ethylcellosolve, etc.), aromatic series (toluene, a xylene, chlorobenzene, etc.), ketones (an acetone, methyl ethyl ketone, etc.), ester solvents (ethyl acetate, butyl acetate, etc.), ether (a tetrahydrofuran, dioxane, etc.), chlorine-based solvents (chloroform, trichloroethylene, etc.), an amide series solvent, dimethyl sulfoxide (dimethylformamide, N-methyl pyrrolidone etc., etc. be mentioned

[0105] The Junji Men ***** applying method with a well-known gravure roll, the extrusion applying method, the wire bar applying method, a roll coating method, etc. are employable as coating from the former.

[0106]

[Example] An example is given to below and this invention is concretely explained to it.

[0107] (Creation of base materials A and B) It rinsed, after being immersed in 5% sodium-hydroxide water solution kept at 65 degrees C in the aluminum plate (construction material 1050, refining H16) with a thickness of 0.24mm and performing indirect desulfurization fat processing for 1 minute. This degreased aluminum plate was rinsed, after being immersed for 1 minute into 10% hydrochloric-acid water solution kept at 25 degrees C and neutralizing.

[0108] Subsequently, the desmut treatment for 10 seconds was performed in 5% sodium-hydroxide water solution kept at 60 degrees C in this aluminum plate after alternating current performed electrolysis surface roughening for 60 seconds on condition that 25 degree C and 100 A/dm² among 1.0% of the weight of the hydrochloric-acid water solution. Anodizing was performed for this surface roughening aluminum plate for 6 minutes on condition that 30 degree C and 4 A/dm² in 40% phosphoric acid solution, silic acid sodium performed sealing further, and the base material was created.

[0109] (Creation of the sensitive material for the lithography versions) On the above-mentioned base material, using the wire bar, the photopolymerization nature constituent coating liquid of the following presentation was applied so that it might become 2.0 micrometers of desiccation thickness, and the sensitization layer was formed.

[0110]

Photopolymerization nature constituent Binder resin (hydroxyethyl methacrylate / methyl methacrylate / butyl acrylate / acrylic-acid =30/50/5/15) 50 weight sections Monomer (dipentaerythritol hexa chestnut rate) 50 weight sections Radical generating agent (A-1) Five weight sections Light-and-heat conversion ingredient (IR-5) Ten weight sections Onium salt (Q-1) Five weight sections Methyl ethyl ketone On the 400 weight sections sensitization layer, 10% water solution of polyvinyl alcohol (Japanese synthetic-chemistry company make: Gosenol GL-05) was applied and dried with the wire bar so that it might become 2.0 micrometers of desiccation thickness, and the protective layer was prepared. The obtained sensitive material was heat-treated under protection from light for 80 degree C and 2 minutes, and it considered as the sensitive material 1 for assessment.

[0111] (Image creation and assessment) Image exposure of the created sensitive material was carried out on condition that the following.

[0112] Light source: LT090MD (the Sharp make, the output of 100mW, dominant wavelength of

830nm)

optical effectiveness: -- 67% exposure beam diameter: -- $1/e^2=10$ micrometer (power density: 85307 W/cm²)

Exposure pitch: In the developer of the following presentations of the sensitive material after 6-micrometer exposure, it was immersed for 45 seconds, and after rinsing what was eluted in the protective layer and the sensitization layer of the unexposed section, it dried and 25 degrees C of images were obtained.

[0113]

Developer presentation Benzyl alcohol The 360 weight sections Diethanolamine The 210 weight sections Pelex NBL The 180 weight sections (Kao make: t-butyl naphthalene sulfonic-acid sodium) Potassium sulfite 90 weight sections Water 3000 weight sections sensibility and shelf life were evaluated as follows.

[0114] The minimum exposure energy (light exposure which can reproduce the line breadth of 10 micrometers) required for <sensibility> image formation was measured. It is high sensitivity, so that a value is small.

[0115] The sensibility after preservation was measured for seven days to RH <shelf-life> 55 degree C and, and 20%. Shelf life is so good that there are few differences with the sensibility before preservation.

[0116] Next, except having changed the presentation of a sensitization layer, as shown in a table 1, the sensitive material 2-20 as well as sensitive material 1 was created, and the image was created and evaluated similarly.

[0117]

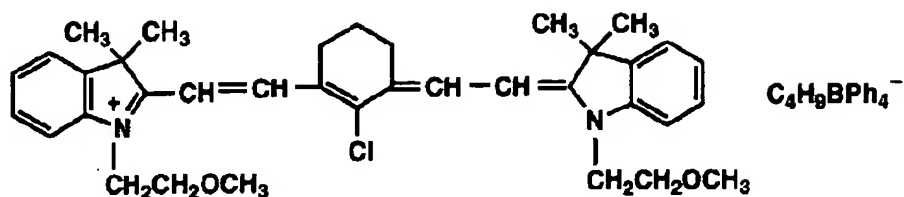
[A table 1]

感光材料No.	光重合 開始剤	オニウム 塩	光熱変換 素子	感度(mJ/cm ²)	
				保存前	保存後
1(本発明)	A-1	QN-1	IR-5	3.1	3.5
2(本発明)	A-1	QN-1	IR-4	2.8	3.2
3(本発明)	A-1	QN-1	IR-13	4.3	4.8
4(本発明)	A-2	QN-1	IR-5	3.3	3.7
5(本発明)	A-3	QN-1	IR-5	3.5	3.9
6(本発明)	A-4	QN-1	IR-5	7.3	7.6
7(本発明)	A-2	QN-1	IR-17	4.2	4.5
8(本発明)	A-3	QN-1	IR-18	4.8	5.1
9(本発明)	A-1	QN-2	IR-22	3.4	3.9
10(本発明)	A-2	QN-3	CB	5.2	5.4
11(本発明)	A-3	QN-16	IR-5	6.1	6.5
12(本発明)	A-1	QS-15	IR-4	6.8	7.5
13(本発明)	A-2	QI-9	IR-5	5.4	5.9
14(本発明)	A-3	QP-1	IR-5	5.9	7.1
15(本発明)	A-4	QP-10	IR-5	6.2	6.8
16(本発明)	A-2	QS-1	IR-5	6.6	7.1
17(本発明)	A-3	QS-8	IR-5	7.0	7.4
18(比較例)	A-1	—	IR-5	85	90
19(比較例)	—	QN-1	IR-5	105	110
20(比較例)	—	—	IR-C	1.1	150

[0118]

[Formula 15]

IR—C



[0119] The result of a table will not show that sensibility is good and the fluctuation after preservation also has it without a radical generating agent and an onium being put together. [little]

[0120]

[Effect of the Invention] The lithography version has been offered using the sensitive material for the lithography version creation which has high sensibility to a near infrared ray field, and was excellent in preservation stability with this invention.

[Translation done.]